Biodegradable Plastics Association

A not-for-profit Association

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Standard Specification for:

Accelerated Stability & Abiotic Degradation Testing of Oxo-Biodegradable Polyethylene and Polypropylene Film Products

Designed to

Degrade Upon Exposure to the Environment as Litter

Version 1.1 – Published June 2018

1.0 INTRODUCTION

1.1 Oxo-biodegradable Plastics

1.1.1 Oxo-biodegradable plastic technology is based on additive systems which promote degradation of polyolefins such as polyethylene and polypropylene (and co-polymers, thereof) via catalysis of the natural oxidative chain-cleavage leading to molecular-weight reduction and oxidation of the polymer. This causes a loss of mechanical properties, oxygen uptake, increased hydrophilicity, and reduced molecular-weight ultimately resulting in a material which is no longer a plastic and can be assimilated into the environment by micro-organisms commonly found on land and in the oceans.

1.1.2 Oxo-biodegradable plastic products are not designed or intended to be littered but are so designed that if they do get into the open environment as litter they will not lie or float around for decades.

1.2 The Oxo-Biodegradable Plastics Association (OPA)

1.2.1 The OPA is a not-for-profit association, which exists to explain how oxo-biodegradable plastics work, and why they are necessary. The OPA wishes to ensure that oxo-biodegradable plastic technology is supplied only by reputable suppliers, who can produce evidence that their products have been tested according to well established Standards, and that they are themselves accredited to ISO 9001 and 14001.

1.3 Validation of Prodegradant Additive Systems

1.3.1 Current international standards, such as ASTM D6954-2018, are well established to demonstrate molecular-weight reduction enabling biodegradation, and to demonstrate the absence of ecotoxicological effects.

1.3.2 The OPA require that suppliers of oxo-biodegradable masterbatch additives demonstrate that plastic products made with their additives meet the requirements of such standards, via testing at competent, independent, and accredited third-party laboratories.

1.3.3 Testing, commissioned by or on behalf of the additive supplier and done according to international standard methods, of representative plastic product sample(s) made with the prodegradant additive formulation representative of that supplied to the market, should demonstrate in accordance with the methods and requirements of relevant national and international standards that:

a) The representative test film made with the prodegradant additive does not contain heavy metals or other substances of concern.

b) The plastic film made with the prodegradant additive undergoes significant molecular weight reduction in accelerated ageing or natural conditions, in a meaningful timeframe.

c) The degraded residues of abiotic degradation undergo biodegradation to a significant extent, in a meaningful time frame.

d) The substrate and products of the biodegradation test (soil or compost and plastic degradation and biodegradation residues) demonstrate no significant ecotoxicological effect.

1.4 Validation of Film Products Marketed as Oxo-Biodegradable

1.4.1 For the purpose of routine validation of examples of finished products made with the additive or masterbatch, testing to show compliance with the international standards mentioned above is prohibitively expensive and time-consuming.

1.4.2 It is therefore the purpose of this Standard specification to establish a set of practical test methods and criteria for the evaluation and validation of abiotic degradation of finished films and articles which are marketed as oxo-biodegradable.

1.4.3 It is not the purpose of this standard to directly demonstrate that the products of abiotic degradation of the test specimen will undergo biodegradation and to demonstrate the absence of ecotoxicological effects.

1.4.4 However, in the case of a film product which:

a) has been formulated and manufactured according to current legislation, with particular respect to environmental and waste legislation which limits or prohibits potentially toxic or harmful components in packaging products;

b) uses a prodegradant additive system in accordance with the suppliers' instructions, which has been demonstrated to promote degradation enabling biodegradation without significant eco toxicological effect (see 1.3.3 above) in representative test samples.

it follows that the product will undergo molecular weight reduction in the environment enabling biodegradation.

1.4.5 Conversely, failure to meet the degradation requirement of this standard shows a product that would remain stable in the environment as litter for a prolonged period of time; and failure to meet the stability requirements of this standard shows a product which is not fit for use, reuse or recycling.

2.0 REFERENCE DOCUMENTS

2.1 ASTM D6954 - Standard Guide for Exposing and Testing Plastics that Degrade in the Environment by a Combination of Oxidation and Biodegradation

2.2 BS 8472 - Method for determining the degradability, biodegradability and non-eco-toxicity of oxo-biodegradable plastics

2.3 ASTM D5510 - Standard Practice for Heat-Aging of Oxidatively Degradable Plastics (Referenced in ASTM D6954 – 2018)

2.4 ASTM D5208 - Standard Practice for Fluorescent Ultraviolet (UV) Exposure of photodegradable Plastics

2.5 ISO 10640 - Plastics -- Methodology for assessing polymer photo-ageing by FTIR and UV/visible spectroscopy

3.0 TERMINOLOGY

General definitions applicable to plastics appear in ASTM D883-11 or CEN TR 15351 or both.

i. Degradation (of plastic), n—a deleterious change in the chemical structure, physical properties, or appearance of a plastic. (D883-11)
ii. ii. Degradable (of plastic) n –a plastic designed to undergo a significant change in its chemical structure under specific environmental conditions resulting in a loss of some properties that may vary as measured by standard test methods appropriate to the plastic and the application in a period of time that determines its classification. (D883 – 11)
iii. Degradability n – the quality of being degradable
iv. iv. Biodegradation (of plastic), n—degradation of a polymeric item as a result of cell-mediated phenomena. (CEN TR 15351)
v. Biodegradable, n – capable of biodegradation
vi. vi. Biodegradability, n - the quality of being biodegradable
vii. Oxidation, n—process promoted thermally or by ultraviolet (UV) radiation or both in the presence of oxygen. (CEN TR 15351)
viii. viii. Oxo-degradation, n—degradation resulting from oxidative cleavage of macromolecules. (CEN TR 15351)
ix. ix. Oxidatively degradable plastic, n—a degradable plastic in which the degradation results from oxidation (D883-11).
x. Oxo-biodegradation, n—degradation resulting from oxidative and cell-mediated phenomena either simultaneously or successively. (CEN TR 15351)
xi. Oxo-biodegradable, n – capable of oxo-biodegradation
xii. Oxo-biodegradable plastic n- a polymer capable of oxo-biodegradation
xiii. Oxo-biodegradability, n - the quality of being oxo-biodegradable
xiv. Plastic(s), n—material that contains as an essential ingredient one or more organic polymeric substances of large molecular weight, is solid in its finished state, and, at some stage in its manufacture or processing into finished articles, can be shaped by flow. (ASTM D883)

4.0 ACRONYMS

i. FT-IR - Fourier-transform infrared spectroscopy
ii. IR - Infrared
iii. HALS - Hindered amine light-stabilizer
iv. HT-GPC - High-temperature gel permeation chromatography
v. vSEC - Size-exclusion chromatography
vi. UV - Ultra-violet light
vii. XRF - X-ray fluorescence (spectroscopy)
viii. ICP-OES - Inductively coupled plasma-optical emission spectroscopy
ix. AAS - Atomic adsorption spectroscopy
x. OD - Optical Density

5.0 SCOPE

5.1 This Standard is intended for use by suppliers of oxo-biodegradable finished-products, manufactures and converters, users, brand owners, governments, industry bodies, and policy makers, for the routine assessment and validation of polyethylene and polypropylene (and their co-polymers) films and articles marketed as oxo-biodegradable.

5.2 Testing according to the methods outlined in this standard will demonstrate the minimum stability necessary for an article to be fit for use and to be reused and recycled, together with the abiotic degradation step which is the critical mechanism by which oxo-biodegradable plastic technology converts non-biodegradable polymers into a material which can be bioassimilated into the environment.

5.3 This Standard is not designed to replace testing (which must be done by the oxo-biodegradable masterbatch suppliers) to demonstrate that oxo-biodegradable plastics made with their technology go on to form residues that are biodegradable, that they do not contain toxic substances or heavy metals, and do not cause ecotoxicological effects in the process of biodegradation.

5.4 This Standard is therefore designed for the routine evaluation of finished films and articles made with an oxo-biodegradable masterbatch which has already been demonstrated by independent testing according to ASTM D6954 to meet the fundamental requirements of oxo-biodegradable plastic technology.

5.5 This Standard is intended in particular for the evaluation and validation of oxo-biodegradable polyolefin films and articles which are designed to degrade rapidly upon exposure to the environment as litter.

5.6 This Standard does not apply to oxo-biodegradable articles which are designed to maintain a substantial period of service life during sunlight exposure, such as agricultural mulch films or products such as garden furniture designed for extended outdoor use. The criteria for such products must be considered separately.

6.0 SUMMARY OF TEST METHODS

6.1 Determination of Prodegradant Content

.1.1 Prior to the commencement of testing, the presence and appropriate concentration of the prodegradant catalyst shall be confirmed by a suitable technique. In the case of prodegradant catalysts based on organic salts of transition metals, this should be by a technique such as x ray fluorescence (XRF) spectroscopy, inductively coupled plasma-optical emission spectroscopy (ICP-OES) or atomic adsorption spectroscopy (AAS).

6.1.2 The absence of any prodegradant catalyst should be similarly confirmed in control samples.

6.1.3 The composition of the prodegradant masterbatch and the formulation of the catalyst may be proprietary and subject to confidentiality. It is therefore not required to disclose or obtain commercially sensitive information in order to confirm the prodegradant content. The results of the prodegradant content may be reported by way of a result statement (i.e. “prodegradant present within specified range”) in order to protect sensitive details regarding the composition of the additive.

6.1.4 Initial demonstration of prodegradant content is recommended (in order not to waste time or money), but is not an essential requirement for complying with this standard specification.

6.2 Accelerated Thermal Ageing

6.2.1 Oxo-biodegradable plastic products must remain stable in storage and in normal use, so that they will remain fit for purpose during their intended service-life and can be reused or recycled. if collected.

6.2.2 Oxo-biodegradable plastics must be designed so that degradation is initiated only when they are exposed in the environment as litter, and not simply designed with inherent instability or ‘designed to fail’ so as to create a product which is unstable in normal storage and use. It is therefore of critical importance that an oxo-biodegradable plastic product be demonstrated to remain stable under thermal-ageing for an initial period.

6.2.3 The accelerated thermal-ageing test is designed to simulate real-time storage and use of the oxo-biodegradable plastic product at ambient temperature under normal conditions of storage and use, but tested over a shorter period of time in the laboratory by exposure to elevated temperatures under controlled conditions. Accelerated thermal-ageing is therefore performed at 70ºC in accordance with ASTM D5510.

6.2.4 It is the responsibility of the finished-product manufacturer to carry out these tests and to perform necessary interpretation in order to determine and warrant the shelf and service-life of an oxo-biodegradable plastic product, having regard to the intended application and the materials used.

6.2.5 Elevating the temperature does not invalidate the test. The relationship between the accelerated exposure period and equivalent period at ambient temperatures may be established via comparison with real-time natural ageing and accelerated ageing at multiple temperatures, and development of an Arrhenius relationship. Refer to ASTM D5510.

6.2.6 Oxo-biodegradable plastic products are designed to suffer rapid degradation when they are exposed to sunlight in the environment as litter. It cannot be expected that plastic litter will always be continuously exposed to sunlight, so products which have become occluded from sunlight, in areas of shade or loosely buried in aerobic soil, must continue to degrade abiotically until they become available to microorganisms for biodegradation.

6.2.7 It is therefore of critical importance that oxo-biodegradable plastic products are shown to undergo continued degradation in darkness after initial exposure to sunlight.

6.3 Fluorescent UV ageing.

6.3.1 The UV exposure test is designed to simulate the real-time exposure of the oxo-biodegradable plastic product to the damaging portion of the spectrum of sunlight known to be responsible for polymer degradation, by exposing it for a shorter period of time in the laboratory to elevated UV radiation intensity and temperature.

6.3.2 Accelerated Fluorescent UV ageing is performed at 50ºC, using UVA 340 lamps set to an irradiance not exceeding 0.89 W/(m2 ·nm) at 340 nm, in accordance with ASTM D5208. Subsequent accelerated thermal ageing is performed at 70ºC in accordance with ASTM D5510.

6.3.3 It is the purpose of this standard to demonstrate the abiotic degradation response of the oxo biodegradable plastic following short exposure to sunlight in the environment.

6.3.4 It is however possible and instructive to compare the response of an oxo-biodegradable plastic to the response of the same type of plastic which is not oxo-biodegradable, both in the laboratory and under natural conditions. Oxo-biodegradable plastics are designed to become biodegradable much more quickly.

6.4 Abiotic Polymer Degradation

6.4.1 Abiotic polymer degradation is assessed by identifying carbonyl functional groups, formed as part of the oxidized products of polymer degradation. Polymer oxidation is observed by transmission FT-IR spectroscopy according to ISO 10640. Specifically, determination of features at 1714cm-1 which correspond to carbonyl functional groups.

6.4.2 The extent of degradation (oxidation) is reported as Carbonyl Optical Density (Equation 1), the increase in infra-red absorbance at 1714 cm^{-1} as a function of path-length (film thickness). In the reporting of Carbonyl Optical density, infrared absorbance is adjusted for thickness so that the extent of degradation of films of any thickness (up to a maximum thickness of 100 µm) may be compared.

Equation 1: **Carbonyl Optical Density**

$$\frac{\Delta \text{IR Abs}_{\text{C=0 1714 cm}^{-1}}}{\text{Thickness } (\mu\text{m})}$$

6.4.3 Since oxidative chain-cleavage is the mechanism by which polymer degradation occurs, it follows that increased carbonyl optical density is strongly indicative of reduced mechanical properties, reduced molecular weight, increased hydrophilicity, and hence biodegradability.

6.4.4 Table 1 shows an approximate guide for evaluating the relative extent of degradation of polyethylene and polypropylene films, based upon determined carbonyl optical density value. This is included for general guidance only.

Table 1: Guide to Approximate Evaluation of the Extent of Degradation of Polyethylene or Polypropylene Films by Determination of Carbonyl Optical Density Transmission FT-IR spectroscopy

Extent of Degradation	Carbonyl Optical Density
No Degradation	0.0000
~50% reduction in mechanical properties (EaB)	0.0010
Spontaneous Embrittlement ~>95% reduction in mechanical properties (EaB)	0.0100
Significant Biodegradability	≥0.0300

6.4.5 While this test may be extended beyond the requirements of this Standard in order to demonstrate continued degradation, it can be difficult in practice (due to friability of materials with a carbonyl optical density-increase greater than 0.0100), to determine continued degradation by conventional FT-IR transmission spectroscopy. Additional equipment, such as an infrared spectroscopy-enabled microscope (micro FT-IR) may be required.

7.0 APPARATUS

i. Digital micrometer
ii. Cutting equipment. Blades, scalpels and cutting mats.
iii. Sample-holders
iv. Laboratory oven (forced convection preferred) in accordance with the requirements of ASTM D5510.
v. Fluorescent UV weathering equipment in accordance with the requirements of ASTM D5208.
vi. Fourier Transform Infra-Red Spectrometer in accordance with the requirements of ISO 10460.

8.0 PROCEDURE

Table 2: Summary of Test Methods & Criteria Test Method Standard Criteria

Test	Method	Standard	Criteria
Characterisation			
Prodegradant Content	Suitable Method XRF, ICP-OES, AAS -	-	Confirm Prodegradant Content (not required, 6.1.2)
Extent of degradation	Carbonyl Optical Density, by Infra-red spectroscopy	ISO 10640	-
Accelerated Ageing			
Thermal Stability	Accelerated thermal ageing	ASTM D5510	Carbonyl OD ≤0.0010, 360 hours
Degradation	Accelerated Fluorescent UV Ageing + Accelerated Thermal Ageing	ASTM D5208 ASTM D5510	Carbonyl OD ≥0.0100, 360 hours (48 UV + 312 Thermal)

8.1 Preparation of Test Specimens

8.1.1 A representative sample of the product to be tested, taken from commercial production, should be presented for testing in the form in which it would be placed on the market. However, the sample may be presented as a film, as it is not necessary to undergo conversion into a plastic bag or other product as this will not affect the composition or form of the product. The product should be provided for testing as soon as possible after production.

8.1.2 If multiple products are to be made from a film, a single sample of the film is representative of all such products.

8.1.3 If multiple products are converted from film produced with the same formulation but with different thicknesses, the thickest of such products shall be submitted for testing and may be considered representative of all such products with an equivalent or lower film thickness.

8.1.4 For the purpose of calculating carbonyl optical density, the thickness shall be precisely measured using a micrometer or thickness gauge.

8.1.5 Where possible a section of film free from printing shall be chosen. The sample shall be dry, clean and free of residue.

8.1.6 Separate sample specimens shall be prepared for accelerated thermal stability (8.3) and (8.4) accelerated degradation tests.

8.1.7 The film sample shall be cut and secured in a suitable sample-holder of dimensions compatible with the intended ageing equipment and FT-IR spectrometer, which allows for recording of the transmission infrared spectrum repeatedly in four discrete locations on the film. The test shall be configured so that the spectrum may be recorded at the same four locations on the sample over the course of the accelerated ageing tests.

Notes on control samples:

For the purposes of comparison with a conventional plastic product, an equivalent conventional plastic control sample may be submitted for testing in parallel with the test specimen which contains the prodegradant additive. The control sample should be of identical formulation in all respects, with the exception of the inclusion of the prodegradant masterbatch (the proportion of the material represented by the prodegradant masterbatch may be substituted by a polymer resin which already forms part of the product formulation). Ideally, the control sample will be produced as part of the same production run as the test specimen, after the production line has been set to optimum processing conditions but prior to the introduction of the prodegradant masterbatch to the production line.

8.2 Polymer Degradation

8.2.1 The initial (t0 hrs) infrared spectrum shall be recorded in quadruplicate for all prepared test specimens prior to the commencement of accelerated stability and degradation tests. The infrared spectrum shall be stored electronically and the average absorbance at 1714cm-1 shall be calculated and recorded. For each sample, the initial average absorbance at 1714cm-1 shall be subtracted from all subsequent average absorbance values in order to yield the total increased in absorbance at 1714cm-1 . The total increase in absorbance at 1714cm-1 will be divided by the film sample thickness to yield carbonyl optical density and will be recorded as a function of exposure time.

8.2.2 Test and control Samples shall be free of degradation at the commencement of accelerated thermal stability and degradation tests. The absence of degradation shall be confirmed by the qualitative evaluation of the initial infra-red spectrum to determine no features in the sample spectrum, centered about 1714cm-1 which correspond to the presence of carbonyl species associated with the products of degradation.

8.3 Thermal Stability Test

8.3.1 The test specimen shall be exposed to accelerated thermal ageing in a laboratory oven at 70ºC in accordance with ASTM D5510. 8.3.2 The test shall be considered successful if the carbonyl optical density value recorded for the test specimen does not exceed 0.0010 after ≥360 hours total accelerated thermal ageing exposure.

8.3.3 It is recommended that the sample is periodically removed from ageing at intervals of 48-96 hours for determination of Carbonyl Optical Density throughout the duration of the test. The sample should be removed from ageing for the shortest time practicable and should returned to ageing within one hour.

8.4 Abiotic Degradation Test

8.4.1 The test specimen shall be exposed to accelerated Fluorescent UV ageing at 50ºC, using UVA 340 lamps set to an irradiance not exceeding 0.89 W/(m2 ·nm) at 340 nm, in accordance with ASTM D5208. After 48 hours the test specimen shall be removed from the equipment.

8.4.2 Within 48 hours of the completion of UV ageing, the carbonyl optical density shall be measured by infrared spectroscopy and recorded, and the sample transferred to accelerated thermal ageing in a laboratory oven, performed at 70ºC in accordance with ASTM D5510.

8.4.3 The initial fluorescent UV exposure is intended to condition the sample by disabling the stabilizers in the prodegradant additive and polymer resin formulations, so as to allow degradation to continue without any further direct sunlight exposure. The initial UV exposure is not designed to promote the onset of oxidative degradation, and it is not necessary or normally expected to observe significant degradation in this part of the test.

8.4.4 The test shall be considered successful if a carbonyl optical density of 0.0100 is reached or exceeded after ≤360 hours total exposure time (inclusive of 48 hours accelerated fluorescent UV exposure and ≤312 hours accelerated thermal ageing).

8.4.5 The sample should be periodically removed from ageing at intervals of 48-96 hours for determination of Carbonyl Optical Density throughout the duration of the test. The sample should be removed from ageing for the shortest time practicable and should returned to ageing within one hour.

9.0 REPORTING

A written and signed report shall state:

i. Product description
ii. Production date
iii. Prodegradant masterbatch supplier
iv. Prodegradant masterbatch formulation/grade identifier
v. Masterbatch addition-rate
vi. Product polymer type/blend
vii. Date sample was received, and date tested
viii. Thickness of all test and control samples tested.
ix. Description of the test equipment used.
x. Test conditions xi. Test Results